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## Catalysis by Oxidic Spinel Ferrites

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**Abstract.** Mixed metal oxides *viz.* ferrites, ferrochromites and chromites have been studied with a view to investigating a correlation between bulk physical properties and catalytic performance over decomposition of alcohols. We could observe a satisfactory relationship between lattice parameter, electronic activation energy, nature and mobility of charge carriers and Curie temperature with reference to catalytic activity of various spinel ferrites.

### 1. INTRODUCTION

Study of oxidic solid solutions as catalysts has been steadily developed over past few years and today a number of industrial establishments are interested in such compounds for commercial applications. Out of various models explaining heterogeneous catalysis one which proposes a relationship between electronic structure of catalysts and catalytic activity [1] was of interest to us. We have therefore investigated number of spinels with reference to their catalytic behaviour.

### 2. EXPERIMENTAL

#### Synthesis and Characterisation of Catalysts

Synthesis of spinel ferrites was carried out using citrate precursor technique to get ultrafine particles ( $\sim 0.65 \mu\text{m}$ ) [2]. The stoichiometric formula of the precursor was estimated to be  $\text{M}_3\text{Fe}_6(\text{Cit})_n\text{nH}_2\text{O}$  (where  $n$  is the number of adsorbed water molecules). The characterisation of various catalysts was done using XRD, DC resistivity, thermo-emf and a.c. susceptibility techniques. Catalytic studies were carried out from 473-673 K using fixed bed flow reactor employing  $\sim 3$  g of powdered catalyst. The products were analysed on GC and confirmed by GCMS.

### 3. RESULTS AND DISCUSSION

#### 3.1 Transport Properties

The catalytic performance data for the decomposition of alcohols at 350°C is summarised in Table 1. We could observe a good correlation between electronic activation energy and catalytic activity in all the compounds. As the catalysis involves transfer of electrons/holes from the surface of the catalyst to substrate molecule and the process is reversible *i.e.* greater the activation energy, the greater will be the energy required for electronic transition resulting in decreased activity of catalyst. Copper ferrite having lowest activation energy shows maximum % conversion. Mobility of charge carriers was calculated using the equation  $\mu = ed^2 v \exp(-\Delta E/kT)/kT$  where  $\Delta E$  = activation energy and  $d$  = jump length of charge carriers. Since mobility involves the rate of exchange of charge carries from surface to probe molecule and therefore greater the mobility, more easily the charge carriers can be exchanged, increasing the % conversion. The compound possessing the highest mobility in a series has shown maximum activity. For *e.g.*  $\text{CuCr}_2\text{O}_4$  ( $\mu = 3.80 \times 10^{-10} \text{ m}^2/\text{V}\cdot\text{sec}$ ) gave 82.0% benzyl alcohol conversion while  $\text{CuFe}_2\text{O}_4$  ( $\mu = 1.24 \times 10^{-7} \text{ m}^2/\text{V}\cdot\text{sec}$ ) yielded 92.0% conversion at 350°C.

### 3.2 Seebeck Measurements and Product Selectivity

It is needless to say that choosing a proper catalyst is essential for product selectivity. The effect of nature of charge carriers on dehydrogenation and dehydration selectivity is presented in Table [1]. A good correlation between dehydrogenation and dehydration selectivity and nature of charge carriers is observed in all the series. Cobalt ferrite, a good p-type semiconductor has shown greater tendency for aldehyde selectivity.

### 3.3 Magnetic Properties and Catalytic Behaviour

Initial susceptibility studies were carried out using a field of 0.5 Oe by a double coil method [3]. From the plots of  $\chi/\chi_i$  vs T, Curie temperatures were determined. From Table [1] it is noted that as magnetic ordering temperature increases conversion also increases which suggests a possible correlation between magnetic ordering and catalytic activity. Further, even after studying large number of spinels, we could not establish any relationship between coercive force and catalytic activity[4].

Table 1 : Lattice constant (a), activation energy ( $\Delta E$ ), Seebeck coefficient ( $\alpha$ ), mobility ( $\mu$ ), Curie temperature ( $T_c$ ), % conversion and % selectivity at 350°C for different spinels.

Sample No.	Compound	'a' A°	$\Delta E$ eV	$\alpha$ ( $\mu$ V/K)	$\mu$ m <sup>2</sup> /Volt sec)	$T_c$ (K)	%Con- version	% Selectivity		Probe molecule
								-one -ald	-ene	
1.	CuFe <sub>2</sub> O <sub>4</sub>	8.37	0.16	-333.33	1.24 X 10 <sup>-7</sup>	490	92	06	73	Benzyl Alcohol
2.	CuFeCrO <sub>4</sub>	8.33	0.25	+100.00	3.89 X 10 <sup>-9</sup>	417	88	70	04	
3.	CuCr <sub>2</sub> O <sub>4</sub>	8.27	0.31	+80.00	3.80 X 10 <sup>-10</sup>	-	82	54	17	
4.	MgFe <sub>2</sub> O <sub>4</sub>	8.37	0.39	-171.42	1.76 X 10 <sup>-11</sup>	680	47	16	79	Cyclo- hexanol
5.	MgFeCrO <sub>4</sub>	8.35	0.49	-083.33	3.78 X 10 <sup>-13</sup>	653	36	30	65	
6.	MgCr <sub>2</sub> O <sub>4</sub>	8.33	0.71	+250.00	7.74 X 10 <sup>-17</sup>	-	22	55	41	
7.	CoFe <sub>2</sub> O <sub>4</sub>	8.36	0.27	+267.00	6.66 X 10 <sup>-10</sup>	785	36	71	28	Benzyl Alcohol
8.	CoFeCrO <sub>4</sub>	8.34	0.47	+093.00	2.10 X 10 <sup>-14</sup>	538	26	54	42	
9.	CoCr <sub>2</sub> O <sub>4</sub>	8.32	0.67	-132.00	3.60 X 10 <sup>-16</sup>	-	11	28	60	
10.	CuMnFeO <sub>4</sub>	8.40	0.42	+070.80	52.9 X 10 <sup>-13</sup>	575	72	83	11	Heptanol
11.	Zn <sub>0.4</sub> Cu <sub>0.6</sub> Mn <sub>0.6</sub> Fe <sub>1.4</sub> O <sub>4</sub>	8.41	0.46	+05.00	11.16 X 10 <sup>-13</sup>	517	49	62	34	
12.	ZnFe <sub>2</sub> O <sub>4</sub>	8.42	0.59	-55.20	7.08 X 10 <sup>-15</sup>	-	23	45	49	

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